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FT-Raman and FT-IR spectra of a fluoroquinolone complex

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Abstract . The fluorinated quinolone complexes possess antibacterial activity Quinoline and napthalene have the same symmetry and orbital structure giving rise to similar skeletal and C-H vibrations The assignments for napthalene, quinoline and 1,4 napthaquinone form the basis for the study of the vibrational frequencies in the FT-Raman and FT-infrared spectrum of 1-ethyl-3-carboxyl-7-hexahydropyrazyl fluoroquinolone The Fourier transform far-IR spectrum of this complex have also been investigated for the various low-lying deformation modes. The molecule assumes C_s point group of symmetry

Keywords : Fourier transform, spectra, fluoroquinolone, assignment.

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The fluoroquinolone complex studied is 1-ethyl-3-carboxyl-7-hexahydropyrazyl fluoroquinolone has antibacterial activity against many gram-positive and gram-negative bacteria like many of the halogen derivatives of quinoline. The structures of quinoline and quinone are similar to that of napthalene except for the aza group and carbonyl substitutions respectively. The orbital structure of quinoline is related to those of pyridine and napthalene. The infrared and Raman spectra of quinoline and isoquinoline have been reported and their assignments have been previously studied (1-4). The structure of the fluoroquinolone complex studied is presented in Figure 1.

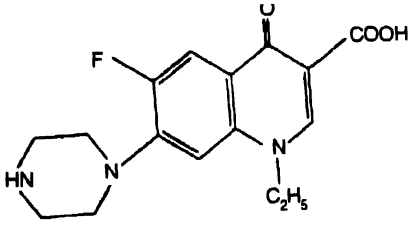

Figure 1. Structure of fluoroquinolone complex (1-ethyl-3-carboxyl-7-hexahydropyrazyl fluoroquinolone)

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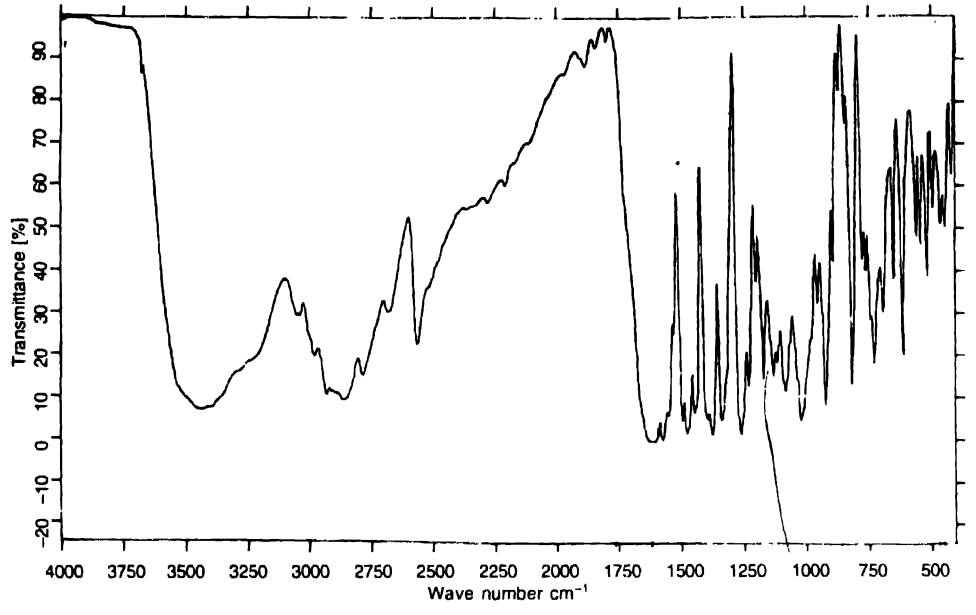
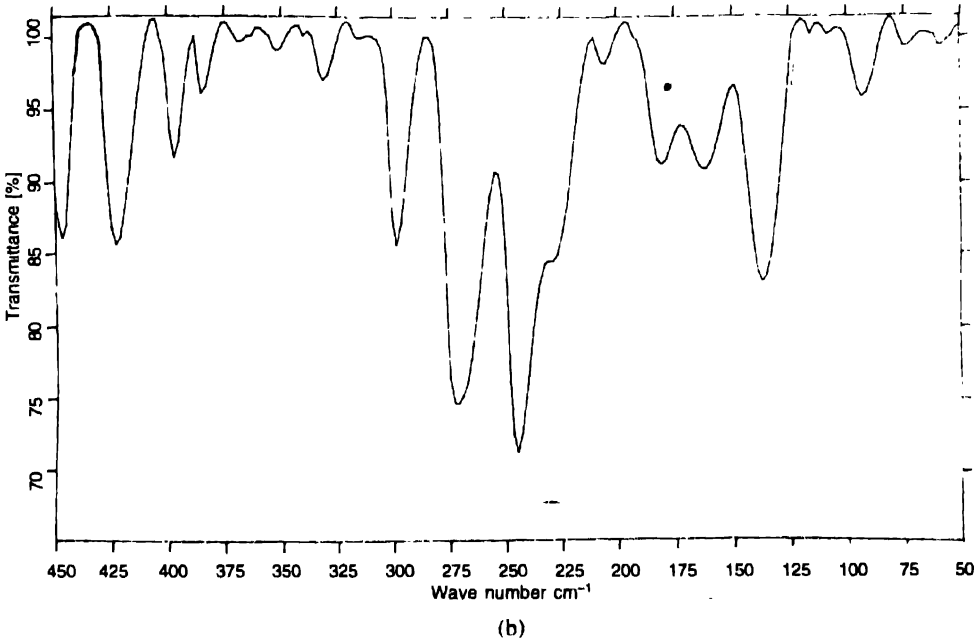
The Fourier transforms infrared spectrum of the fluoroquinolone complex was recorded on a Bruker IF 66v spectrometer in the range 4000-400 cm^{-1} using KBr pellet techniquc is presented in Figure 2(a) and its far-IR spectrum recorded in the range 450-50 cm^{-1} using



(a)



(b)

Figure 2. (a) FT-IR, (b) FT far-IR spectrum of a fluoroquinolone complex (1-ethyl-3-carboxyl-7-hexahydropyrazyl fluoroquinolone).

polyethylene pellet technique in Figure 2(b). The Fourier transform Raman spectrum of the same compound recorded on FT-IR spectrometer using FRA 106 Raman module in the range 3500-200 cm^{-1} employing powder technique is presented in Figure 3. The observed frequencies,

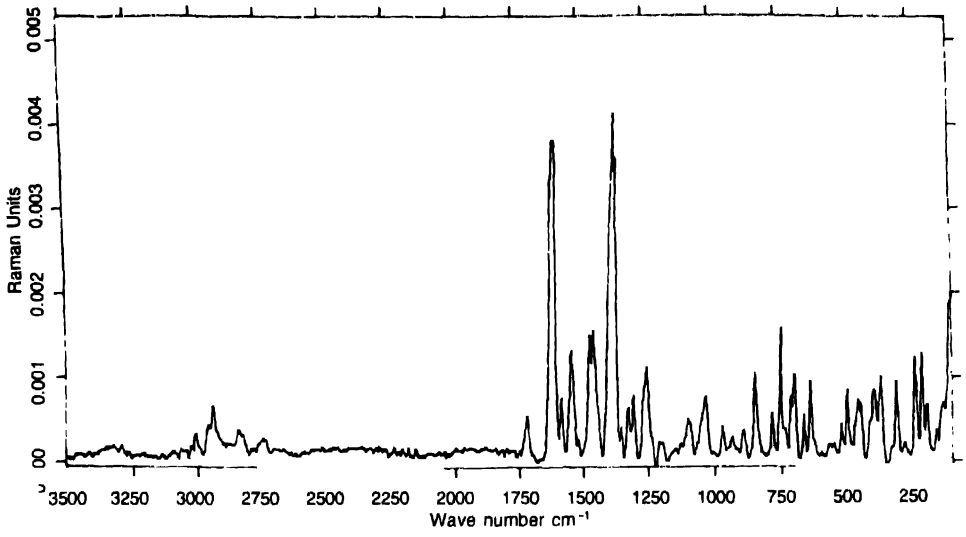


Figure 3. FT-Raman spectrum of a fluoroquinolone complex (1-ethyl-3-carboxyl-7-hexahydropyrazyl fluoroquinolone)

relative intensities, symmetry species of molecular frame work and the probable assignments of the molecule have been summarized in Table 1.

Table 1. Vibrational Assignment for fluoroquinolone complex molecule (1-ethyl-3 carboxyl-7-hexahydropyrazyl fluoroquinolone)

Infrared Frequency (cm^{-1})	Raman Frequency (cm^{-1})	Symm Species	Assignment
59 (VW)			Lattice
74 (VW)			Lattice
92 (VW)			Lattice
108 (VW)		A"	Ring distortion
116 (VW)			COOH torsion
135 (W)	135 (19)	A"	C-COOH bend o p
161 (VW)		A'	Wing Wagging
179 (VW)		A"	NCC deformation o p
205 (VW)	198 (13)	A"	Skeletal deformation o p , C-COOH bend i.p
	216 (26)	A"	N-C_2H_5 bend o.p
239 (W)	241 (24)	A"	C = O bend o.p.
267 (W)		A'	C-COOH stretching
295 (W)			C-CH_3 bending o.p. (C_2H_5 gr.)
314 (VW)	314 (19)	A"	C-F bending o.p.
330 (VW)		A'	CNC deformation i.p.

Table 1. (cout'd)

Infrared Frequency (cm^{-1})	Raman Frequency (cm^{-1})	Symm Species	Assignment
351 (VW)		A"	Skeletal deformation i.p.
368 (VW)	369 (20)	A'	N-C_2H_5 bend i.p., CNC deformation i.p.
384 (VW)			C-CH_3 bending i.p (C_2H_5 gr.)
395 (VW)	400 (16)	A"	Skeletal deformation o.p.
420 (W)		A'	NCC deformation i.p
448 (W)	456 (15)	A'	C = O bending i p.
465 (W)		A'	NCC deformation i.p.
497 (W)	499 (17)	A"	Skeletal deformation i p.
522 (M)	522 (11)	A'	Skeletal deformation i.p , C = O bending o p (COOH gr.)
548 (M)		A'	Skeletal deformation i.p
566 (M)		A'	Skeletal deformation i.p
624 (M)		A'	Skeletal deformation i.p
	639 (21)		C = O bending i p (COOH gr.)
659 (W)	665 (12)	A'	Skeletal deformation i.p
705 (M)	700 (21)	A'	C -F bending i.p
738 (VS)		A"	Skeletal deformation o p
767 (M)	753 (33)	A'	Ring breathing
784 (M)	784 (12)	A'	Skeletal deformation o.p
828 (VS)		A"	C-H bending i p
850 (VW)	849 (22)	A"	C-H bending o.p., N-H bend o p
882 (VW)		A'	C-N stretch
902 (M)	892 (9)	A"	C-H bending o p
932 (VS)	934 (7)	A"	C-H bending o p
955 (W)		A'	C-H bending o p
	970 (9)	A"	C-H bending o p
1032 (VS)	1035 (17)	A'	C-H bending i.p.
1093 (VS)			CH_3 Rocking (C_2H_5 gr.)
	1101 (12)	A'	C-H bending i.p
1116 (VS)		A'	N-C_2H_5 stretching, C-H bending i.p.
1133 (VS)		A'	C-H bending i.p
1180 (VS)		A'	C-N stretch
	1209 (6)	A'	C-F stretching
1221 (M)		A'	C-N stretching
1233 (VS)		A'	C-H bending i.p.
	1256 (19)	A"	C-H bending i.p.
1269 (VS)		A"	C-C ring stretch
	1305 (17)	A'	C-C ring stretch
	1328 (13)	A'	C-C ring stretch, C-N stretch
1348 (VS)	1353 (9)	A'	C-N ring stretch

Table 1. (cout'd)

Infrared Frequency (cm^{-1})	Raman Frequency (cm^{-1})	Symm Species	Assignment
1383 (VS)		A"	C-C ring stretch
	1398 (84)	A'	C-C stretch,CH_3 symmetric bending (C_2H_5 gr)
1422 (VS)			CH_2 Symmetric bending (C_2H_5 gr)
	1460 (32)	A'	C-C ring stretch, C-N stretch
1473 (VS)	1475 (31)		CH_3 and CH_2 asymmetric bending (C_2H_5 gr)
1486 (VS)		A'	C-C ring stretch
1517 (VS)		A'	C-C ring stretch
1526 (S)		A'	C-C ring stretch
	1546 (27)	A'	C-C ring stretch
1584 (VS)	1584 (18)	A'	C-C ring stretch
1620 (VS)	1625 (77)	A"	C-C ring stretch, N-H bend i.p
	1723 (12)		C = O stretch, (COOH gr.)
1800 (VW)			1233 + 566
1833 (VW)			1113 + 705
1883 (VW)			1032 + 850
2116 (W)			1180 + 932
2199 (VW)			1526 + 624
2283 (W)			1584 + 705
2552 (S)			1517 + 1032
2682 (M)			1584 + 1093
	2752 (6)		1546 + 1209
2784 (S)			1517 + 1269
2850 (VS)	2847 (8)		CH_2 symmetric C-H stretch (C_2H_5 gr)
2885 (VS)			CH_3 symmetric C-H stretch (C_2H_5 gr)
	2946 (15)		CH_2 asymmetric C-H stretch (C_2H_5 gr.)
2980 (VS)			CH_3 asymmetric C-H stretch (C_2H_5 gr)
3040 (S)	3010 (7)	A'	C-H stretch
3290 (S)	3296 (5)	A'	N-H stretching
3433 (VS)			O-H stretching

Number within parantheses are relative intensities

VS- Very Strong, S- Strong, M- Medium, W- Weak, VW- Very Weak, i.p.- in-plane, o.p -out-of-plane

Skeletal vibrations :

The assignments of the frequencies for the fluoroquinolone complex molecule (FQ) is based on a comparative study of the fundamental vibrations of quinoline, naphthalene (5-7) and 1,4 napthaquinone (NQ)(8) molecules. Napthalene and quinoline belong to D_{2h} point group and 1,4-napthaquinone belongs to C_{2v} point group, while the FQ molecule has C_s point group of symmetry. The Raman active C-C ring stretching vibrations of FQ molecule at 1584 cm^{-1} and 1460 cm^{-1} corresponds to two of the three Ag modes in napthalene at 1579 cm^{-1} and 1460 cm^{-1} ; in quinoline at 1571 cm^{-1} and 1471 cm^{-1} ; In NQ molecule at A_1 (1588 cm^{-1}) and A_1 (1453

cm^{-1}). The high intensity of the 1460 cm^{-1} band compared to quinoline is due to the additional C-N ring stretching vibration present at this frequency. The Raman active 1625 cm^{-1} frequency of FQ molecule corresponds to the B_{3g} mode at 1624 cm^{-1} in napthalene ; 1619 cm^{-1} in quinoline; and B_2(1605 cm^{-1}) mode in NQ molecule. The N-H bending vibration has enhanced the intensity of this mode. The infrared active C-C stretching modes of napthalene are at B_{1u} (1595 cm^{-1}), B_{2u} (1509 cm^{-1}), B_{1u} (1387 cm^{-1}) and B_{1u} (1265 cm^{-1}) ; in quinoline at 1593, 1500, 1392, and 1256 cm^{-1} ; and in NQ molecule at A_1 (1583 cm^{-1}) B_2 (1506 cm^{-1}), B_2 (1335 cm^{-1}), and B_2(1267 cm^{-1}). For the FQ molecule the vibrations at 1584, 1517, 1383 and 1269 cm^{-1} have been identified to these modes. The skeletal in-plane deformation vibrations for napthalene molecule at A_g (514 cm^{-1}), B_{3g} (506 cm^{-1}), B_{2u} (618 cm^{-1}), and B_{1u} (362 cm^{-1}) ; in quinoline at A_g (521 cm^{-1}), B_{3g} (479 cm^{-1}), B_{2u} (611 cm^{-1}), and B_{1u} (377 cm^{-1}) have corresponding vibrations for the FQ molecule occurring at 522 cm^{-1}, 499 cm^{-1}, 624 cm^{-1} and 351 cm^{-1}. However, these vibrations are less intense in comparison with quinoline. The out-of-plane skeletal deformation vibrations for the FQ molecule assigned to about 400 cm^{-1} and 200 cm^{-1} agree with the assignment in NQ molecule at A_2 (410 cm^{-1}) and A_2 (202 cm^{-1}). The two other bands of this mode of vibration at 738 cm^{-1} and 784 cm^{-1} agree with the assignments of napthalene at A_u (740 cm^{-1}) and B_{3u} (780 cm^{-1}) ; 741 cm^{-1} and 786 m^{-1} in quinoline. The skeletal ring breathing vibration of napthalene occurs at 766 cm^{-1} ; in quinoline at 760 cm^{-1} and at 688 cm^{-1} for the NQ molecule with corresponding vibration for the FQ molecule being the high intensity Raman band at 753cm^{-1}.

The intense absorption at 3040 cm^{-1} and the 3010 cm^{-1} Raman band corresponds to C-H mode in the FQ molecule. The Raman active C-H in-plane bending modes for the FQ molecule at 1101 cm^{-1} and 1256 cm^{-1} correspond to the A_g (1114 cm^{-1}), B_{3g} (1240 cm^{-1}) in napthalene , A_g(1140cm^{-1}), B_{3g} (1192 cm^{-1}) in quinoline ; and A_1 (1120cm^{-1}), B_2 (1235 cm^{-1}) in NQ molecule The infrared active C-H in-plane bending modes for FQ are at frequencies 1233, 1133, 1116, 1032 and 828 cm^{-1} whose corresponding vibrations are at 1209, 1144, 1125, 1008, and 810 cm^{-1} in napthalene ; in quinoline these vibrations are at 1216, 1118, 1013 and 785 cm^{-1}. The C-H out-of plane bending vibrations for FQ molecule have been assigned to the frequencies at 970, 934 and 892 cm^{-1} in the Raman spectrum and at 955 and 850 cm^{-1} in the IR spectrum. These modes correspond to B_{2g} (980 cm^{-1}), B_{3g} (938 cm^{-1}), B_{2g}(875 cm^{-1}), B_{3u} (955 cm^{-1}) and A_u (841 cm^{-1}) modes of napthalene molecule. The wing wagging motion is an IR active out-of plane skeletal vibration found to occur in napthalene at 176 cm^{-1} ; in quinoline at 178 cm^{-1} ; and in NQ molecule at 152 cm^{-1}, while for the FQ molecule it is assigned to 161 cm^{-1}. The lattice vibration of the FQ molecule at 92, 74 and 59 cm^{-1} compare well with those of crystalline napthalene at 98,66 and 53 cm^{-1} respectively. The two skeletal C-N ring stretching vibrations of FQ molecule at 1353 cm^{-1} and 1221 cm^{-1} correspond to the frequencies observed for quinoline, which is in place of the two B_{2u} C-C stretching modes of napthalene.

Group vibrations :

The internal vibrations of the C_2H_5 group are those of CH_2 and CH_3 vibrations which give rise to good group frequencies and can be assigned without much difficulty. The methyl rocking vibration is a strong to medium intensity band but usually affected by substitutions has been assigned to 1093 cm^{-1}. [9-11] The N-C_2H_5 stretching and bending vibration have been assigned to 1116 cm^{-1}, 316 cm^{-1} for the in-plane and 216 cm^{-1} for the out-of-plane modes. The C-CH_3 in-plane and out-of-plane bending modes have been assigned to 384 cm^{-1} and 295 cm^{-1} respectively. These assignments and the assignments for the C_2H_5 internal group have been made in comparison with other ethyl substituted aromatic molecules [11-13].

The carboxylic group vibrations have been assigned in comparison with studies made on compounds with carboxylic groups [14-16]. The C-COOH stretching occurs at about 260 cm^{-1} in many compounds and for the FQ molecule this mode has been assigned to 267 cm^{-1}. The in-plane and out-of-plane C-COOH bendings occur at about 201 cm^{-1} and 134 cm^{-1} respectively. The characteristic C = O stretching vibration of the carboxylic group is at 1723 cm^{-1} occurs without much shift ; C = O in-plane bending at 639 cm^{-1} and its out-of-plane bending at 522 cm^{-1} compare well with the spectral studies of COOH related compounds. The carbonyl bending of FQ molecule have been assigned in comparison with the assignments of NQ molecule and p – benzoquinone [17] to 452 cm^{-1} for the in-plane and 240 cm^{-1} for the out-of-plane vibration.

Other vibrations :

The C-F stretchings are generally observed in the region around 1200 cm^{-1} in fluorinated benzenes [18] and for FQ molecule it is the Raman active band at 1209 cm^{-1}. The IR and Raman active vibrations at 700 cm^{-1} and 314 cm^{-1} correspond to C-F in-plane and out-of-plane bending modes respectively. The N-H stretching vibration at 3296 cm^{-1} and its in-plane bending at 1625 cm^{-1} are the other vibrations of the FQ molecule [19]. The N-H out-of-plane bending assigned to 850 cm^{-1} agree with the assignments made for succinimide [20].

Other skeletal vibrations :

The other C-N ring stretchings due to the non-aromatic heterocyclic substitutions in FQ molecule at 1460 cm^{-1} and 1328 cm^{-1} agree with benzamide [21] while the vibration at 1180 cm^{-1} and 882 cm^{-1} agree with the assignments in diacetamide [22]. The substituent has skeletal stretches at 1546, 1526, 1486 and 1328 cm^{-1} and skeletal deformations at 655 and 639 cm^{-1}. The NCC deformations have been assigned to 465, 420 and 179 cm^{-1} corresponding to in-plane and out-of-plane deformations The CNC deformation vibration have been assigned to the frequencies at 369 and 330 cm^{-1}.

A complete vibrational assignment for the fluoroquinolone complex molecule (FQ) has been made in comparison with the assignments of napthalene, quinoline and 1,4 napthaquinone assuming C_s point group of symmetry. The vibrations belongings to the various substituent groups in the complex have been analyzed with respect to similar groups in other molecules.

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